PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

NOVEMBER 2000 SAMPLING EVENT

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Pesticide Monitoring Project Report
November 2000 Sampling Event

Executive Summary

As part of the District's quarterly ambient monitoring program, unfiltered water and sediment samples from 36 sites were collected from November 13 to November 16, 2000, and analyzed for over sixty pesticides and/or products of their degradation. The herbicides ametryn, atrazine, bromacil, hexazinone, norflurazon, and simazine, along with the insecticides/degradates atrazine desethyl, atrazine desisopropyl, alpha endosulfan, ethion, and ethoprop, were detected in one or more of these surface water samples. The ethion concentration of 0.026 µg/L at S99 exceeds the chronic toxicity level (0.003 µg/L) for *Daphnia magna* calculated according to promulgated procedure (FAC 62-302.200). *Daphnia magna* is a sensitive indicator species for aquatic macroinvertebrates. At this level, long term exposure can cause adverse effects on macroinvertebrate species, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long term average exposures.

The herbicide ametryn, together with the insecticides/degradates aldrin, DDD, DDE, DDT, and ethion, were found in the sediment at several locations, along with one PCB compound. Some of the detected sediment concentrations of aldrin, DDD, DDE, DDT, and the PCB compound are usually associated with the potential for impacting wildlife when compared to coastal sediment quality assessment guidelines. One of the DDT and two of the DDD detections were of a magnitude considered to represent significant and immediate hazard to aquatic organisms in coastal sediments. However, there are no corresponding freshwater sediment quality assessment guidelines to further evaluate potential hazards at the District's sampling sites.

The compounds and concentrations found are typical of those expected from intensive agricultural activity.

Background and Methods

The District's pesticide monitoring network includes stations designated in the Everglades National Park Memorandum of Agreement, the Miccosukee Tribe Memorandum of Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimable) waters, while Lake Okeechobee is protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Sixty-five pesticides and degradation products were analyzed for in samples from all of the 36 sites (Figure 1). The analytes, their respective minimum detection limits (MDL), and practical quantitation limits (PQL) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee Florida. The reader is referred to the *Quality Assurance Evaluation* section of this report for a

summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FGWGC) (FDEP, 1994a) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, dermal uptake). Primary ground water standards are enforceable ground water standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the USEPA under Section 304 (a) of the Clean Water Act, if available, or the lowest EC_{50} or LC_{50} reported in the summarized literature. Sediment concentrations are compared to coastal sediment quality assessment guidelines (FDEP, 1994b), as there are no corresponding freshwater sediment quality assessment guidelines. A value below the threshold effects level (TEL) should not have an impact on wildlife. The value between the TEL and probable effects level (PEL) has a possibility for impacts, while those exceeding the PEL have a substantial probability for impacting wildlife. This summary covers surface water and sediment samples collected between November 13 to November 16, 2000.

Findings and Recommendations

At least one pesticide was detected in surface water at 27 of the 36 sites and in sediment at 16 of the 33 sites. Sediment samples are not routinely collected at GORDYRD and CR33.5T. Field staff were not able to obtain a sediment sample at S9. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All these compounds have previously been detected in this monitoring program.

The ethion concentration of 0.026 µg/L at S99, exceeds the chronic toxicity level (0.003 µg/L) for *Daphnia magna* calculated according to promulgated procedure (FAC 62-302.200). *Daphnia magna* is a sensitive indicator species for aquatic macroinvertebrates. At this level, long term exposure can cause adverse effects on macroinvertebrate species, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long term average exposures. Since April 1996, nine out of nineteen sampling events at S99 had a detectable level of ethion in the surface water (Figure 2). With the method detection limit around 0.02 µg/L, any detection will automatically exceed the calculated chronic toxicity (0.003 µg/L) for *Daphnia magna*.

Only alpha (α) endosulfan was detected in the surface water at four locations in the South Miami-Dade farming area during this sampling event (Table 2). However, none of the concentrations exceeded the Florida Class III surface water quality standard (Chapter 62-302) (Figure 3). Endosulfan was not quantified in the sediment at any of the sampling locations.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long term or chronic toxicity impacts are also reported based on the single

sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 µg/L (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC_{50} of 14.1 mg/L for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.010 to 0.062 µg/L. Using these criteria, these surface water levels should not have an acute, detrimental impact on fish or aquatic invertebrates. The sediment concentrations ranged from 4.7 to 21 µg/Kg. However, no sediment quality assessment guidelines have been developed for ametryn.

Aldrin: Aldrin is a non-systemic insecticide with contact, stomach, and respiratory action, used primarily to control soil insects. Its use and manufacture has been discontinued in the United States. Environmental fate and toxicity data in Tables 4 and 5 indicate that aldrin (1) is relatively toxic to mammals and fish; and (2) due to the large hydrophobicity of this compound, results in a significant bioaccumulation factor. Sediment quality assessment guidelines have been developed for several metals and organic compounds in coastal sediments (FDEP, 1994b). The TEL is 0.72 µg/Kg and the PEL is 4.3 µg/Kg for aldrin in coastal sediments. The one aldrin concentration detected (0.83 µg/Kg at ACME1DS) is between the TEL and PEL. The levels between the TEL and PEL have the possibility for impacting wildlife as they have exceeded the threshold level. No surface water detections of aldrin were found.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 µg/L for bluegill and fathead minnow (Verschueren, 1983). Atrazine inhibits cell multiplication of the alga, *Microcystis aeruginosa*, at 3 µg/L and most other biological effects occur at higher concentrations (Verschueren, 1983). The atrazine surface water concentrations found in this sampling event at 16 of the 36 sampling locations, ranged from 0.010 to 1.4 µg/L. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates. Atrazine was not quantified in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA +

DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio, on a molar basis, (DAR) has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). Since none of the sites with observed flow had both atrazine and DEA detected, no comparison can be made for DAR based on flow versus no flow (Table 6). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the south Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (1.5 µg/L). Using these criteria, these levels should not have an acute or chronic detrimental impact on fish. Bromacil was not quantified in the sediment.

DDE, DDD, DDT: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2,2-bis(4-chlorophenyl)-1,1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the USEPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds accounts for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioaccumulation factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

Sediment quality assessment guidelines have been developed for several metals and organic compounds in coastal sediments (FDEP, 1994b). The TEL is 2.1 µg/Kg and the PEL is 374 µg/Kg for DDE in coastal sediments. The majority of the DDE concentrations detected (1.4 to 260 µg/Kg) are between the TEL and PEL. The levels between the TEL and PEL have the possibility for impacting wildlife as they have exceeded the threshold level.

The DDD concentrations detected range from 3.0 to 64 µg/Kg. Those values, which are between the TEL (1.2 µg/Kg) and PEL (7.8 µg/Kg), have the possibility for impacting wildlife. Two of the values (34 µg/Kg at S5A, and 64 µg/Kg at S6) exceed the PEL and are considered to represent significant and immediate hazard to aquatic organisms.

One of the DDT concentrations detected (8.5 µg/Kg at S6) exceeds the PEL (4.8 µg/Kg). This level is considered to represent a significant and immediate hazard to aquatic organisms.

Ethion: Ethion is a non-systemic acaricide and insecticide registered for use on several fruits, citrus, and vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that ethion (1) is strongly sorbed to soil and therefore can accumulate in sediments; (2) is slightly toxic to mammals, relatively toxic to fish and extremely toxic to Daphnia; and (3) bioconcentrates to a limited extent. Several sources of toxicity information have shown both agreement and disagreement of these laboratory tests. The ethion concentrations of 0.026 µg/L at S99, exceeds the chronic toxicity level (0.003 µg/L) for *Daphnia magna* calculated according to promulgated procedure (FAC 62-302.200). *Daphnia magna* is a sensitive indicator species for aquatic macroinvertebrates. At this level, long term exposure can cause impacts to macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long term average exposures. Since April 1996, nine out of nineteen sampling events at S99 had a detectable level of ethion in the surface water (Figure 2). With the method detection limit around 0.019 µg/L, any detection will automatically exceed the calculated chronic toxicity (0.003 µg/L) for *Daphnia magna*.

Ethion was also detected in the sediment at S99 (9.2 µg/Kg). However, no sediment quality assessment guidelines have been developed for ethion.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, the α (alpha) and the β (beta) forms. Endosulfan is highly toxic to mammals, with an acute oral LD_{50} for rats of 70 mg/kg (Hartley and Kidd, 1987). The Soil Conservation Service rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4). β-endosulfan's water solubility and Henry's constant indicate volatilization may be significant in shallow waters. A bioconcentration factor of 1,267 indicates a low to moderate degree of accumulation in aquatic organisms (Lyman et al., 1990). Endosulfan (α only) was detected at four locations in the south Miami-Dade farming area (Table 3). However, none of the concentrations exceeded the Florida Class III surface water quality standard (Chapter 62-302) (Figure 3). Endosulfan was not quantified in the sediment at any of the sampling locations.

Ethoprop: Ethoprop is a non-systemic soil insecticide/nematicide used on many crops including potatoes, tomatoes, sugarcane and turf. Environmental fate and toxicity data in Tables 4 and 5 indicate that ethoprop (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is moderately toxic to mammals and relatively non-toxic to fish; and (3) does not bioconcentrate significantly. Aquatic invertebrate LC_{50} toxicity ranges from 13 µg/L to 25.3 µg/L for ethoprop (U.S. Environmental Protection Agency, 1985). The only surface water concentration of ethoprop found in this sampling event was 0.041 µg/L at S6. This concentration is below a level that would have an acute detrimental impact on fish or aquatic invertebrates.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching,

with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/l for *Daphnia magna* (U.S. Environmental Protection Agency, 1988). The highest surface water concentration detected in this sampling event at S140 (0.061 µg/L) should not have an acute impact on fish or aquatic invertebrates. Hexazinone was not detected in the sediment.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.020 to 0.74 µg/L. Even at the highest concentration, this is over two orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates.

PCBs: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1254 is a commercial grade mixture containing 54% chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. Florida sediment quality assessment guidelines has been developed for total PCBs in coastal sediments (FDEP, 1994b). However, an evaluation of the reliability of the sediment quality assessment guidelines for total PCBs suggests a low degree of confidence can be placed on these guidelines due to the insufficient data used in their development. The TEL is 21.6 µg/Kg and the PEL 189 µg/Kg for PCB's. The sediment residue detected at S190 (28 µg/Kg) and S79 (170 µg/Kg) has a possibility for impacting wildlife. None of the PCB congeners were detected in the surface water.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. Environmental Protection Agency, 1984). The highest surface water concentration of simazine was detected at S5A (0.27 µg/L), below any level of concern for fish or aquatic invertebrates. No simazine was detected in the

sediment.

Quality Assurance Evaluation

Five duplicate samples were collected at sites S176, S38B, S7, S2, and S235. All the analytes detected in the surface water had precision ≤30% RPD. No analytes were detected in the field blanks collected at S142, S6, and S4. No analytes were detected in the three equipment blanks performed at S18C, L3BRS, and S99. All samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. The organochlorine parameters, as well as norflurazon and simazine, failed precision measurements (relative percent difference) for the surface water samples at the following locations: S99, S80, S3, S4, FECSR78, S65E, S191, S79, S78, S235 (including field duplicate), US4125, S12C, S31, S331, and G211. The matrix spike recoveries for these same samples for aldrin, delta-BHC and endrin aldehyde did not meet the specified requirements. The matrix spike recoveries for imidacloprid at S99 (including equipment blank), GORDYRD, S80, S2 (including field duplicate), S3, S4, FECSR78, S65E, S191, S79, CR33.5T, S78, and S235 (including field duplicate) did not meet the specified requirements. The percent recovery of the lab fortified blank for the majority of the organochlorine analytes failed appropriate criteria at: S140, G123, S142 (including field blank), S38B (including field duplicate), L3BRS (including equipment blank), ACME1DS, G94D, S190, S8, S7, (including field blank), S6 (including field blank), and S5A. The remainder of the analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the U.S. Environmental Protection Agency with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect.

Glossary

LD_{50}: The dosage which is lethal to 50% of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LC_{50}: A concentration which is lethal to 50% of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

EC_{50}: A concentration necessary for 50% of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Koc: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:
The ratio of the concentration of a contaminant in an aquatic organism to the

concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:
The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

MDL: The minimum concentration of an analyte that can be detected with 99% confidence of its presence in the sample matrix.

PQL: The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQL is further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15%. In general, the PQL is 2 to 5 times larger than the MDL.

TEL: The threshold effects level represents the upper limit of the range of sediment contaminant concentrations dominated by no effect data entries, or the minimal effects range. Within this range, concentrations of sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms

PEL: The probable effects level was calculated to define the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects or the lower limit of the probable effects range. Within the probable effects range, concentrations of sediment-associated contaminants are considered to represent significant and immediate hazards to aquatic organisms.

References

Adams, C.D., E.M. Thurman. (1991). *Formation and Transport of Deethylatrazine in the Soil and Vadose Zone*. J. Environ. Qual. Vol. 20 pp. 540-547.

Callahan, M.A., M.W. Slimak, N.W. Gabel, I.P. May, C.F. Fowler, J.R. Freed, P. Jennings, R.L. Durfee, F.C. Witmore, B. Maestri, W.R. Mabey, B.R. Holt, and C. Gould. (1979). *Water-Related Environmental Fate of 129 Priority Pollutants, Volume I.* USEPA 440/4-79-029a.

Florida Department of Environmental Protection (1994a). *Florida Ground Water Guidance Concentrations*. Tallahassee, FL.

_____ (1994b). *Approach to the Assessment of Sediment Quality in Florida Coastal Waters, Volume I – Development and Evaluation of Sediment Quality Assessment Guidelines*; prepared by MacDonald Environmental Sciences, Ltd. Ladysmith, British Columbia.

Goolsy, D.A., E.M. Thurman, M.L. Pomes, M.T. Meyer, and W.A. Battaglin. (1997). *Herbicides and Their Metabolites in Rainfall: Origin, Transport, and Deposition Patterns across the*

Midwestern and Northeastern United States, 1990-1991. Environ. Sci. Technol. Vol. 31, No. 5, pp. 1325-1333.

Goss, D. and R. Wauchope. (Eds.) (1992). *The SCS/ARS/CES Pesticide Properties Database: II Using It With Soils Data In A Screening Procedure*. Soil Conservation Service. Fort Worth, TX.

Hartley, D. and H. Kidd. (Eds.) (1987). *The Agrochemicals Handbook.* Second Edition, The Royal Society of Chemistry. Nottingham, England.

Johnson, W.W. and M.T. Finley. (1980). *Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates*. U.S. Department of the Interior, Fish and Wildlife Service Resource Publication 137. Washington, DC.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990). *Handbook of Chemical Property Estimation Methods*. American Chemical Society, Washington, DC.

Mayer, F.L. and M.R. Ellersieck. (1986) *Manual of Acute Toxicity: Interpretation and Database for 410 Chemicals and 66 Species of Freshwater Animals*. United States Fish and Wildlife Service, Publication No. 160

Montgomery, J.H. (1993). *Agrochemicals Desk Reference: Environmental Data*. Lewis Publishers. Chelsa, MI.

Schneider, B.A. (Ed.) (1979). *Toxicology Handbook, Mammalian and Aquatic Data, Book 1: Toxicology Data*. U.S. Environmental Protection Agency. U.S. Government Printing Office. Washington, DC. EPA-5400/9-79-003

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., and Kolpin, D.W. (1992). *A Reconnaissance Study of Herbicides and Their Metabolites in Surface Water of the Midwestern United States Using Immunoassay and Gas Chromatography/Mass Spectrometry*. Environ. Sci. Technol., Vol. 26, No. 12. pp. 2440-2447.

U.S. Environmental Protection Agency (1972).). *Effects of Pesticides in Water: A Report to the States*. U.S. Government Printing Office. Washington, D.C.

_____ (1977). *Silvacultural Chemicals and Protection of Water Quality*. Seattle, WA. EPA-910/9-77-036.

_____ (1984). Chemical Fact Sheet for Simazine. March, 1984.

_____ (1985) Chemical Fact Sheet for Ethoprop. February, 1985.

_____ (1988). Chemical Fact Sheet for Hexazinone. September, 1988.

_____ (1991) Pesticide Ecological Effects Database, Ecological Effects Branch, Office of

Pesticide Programs, Washington, DC.

_____ (1996). *Drinking Water Regulations and Health Advisories*. Office of Water. EPA 822-B-96-002.

Verschueren, K. (1983). *Handbook of Environmental Data on Organic Chemicals*. Second Edition, Van Nostrand Reinhold Co. Inc. New York, NY.

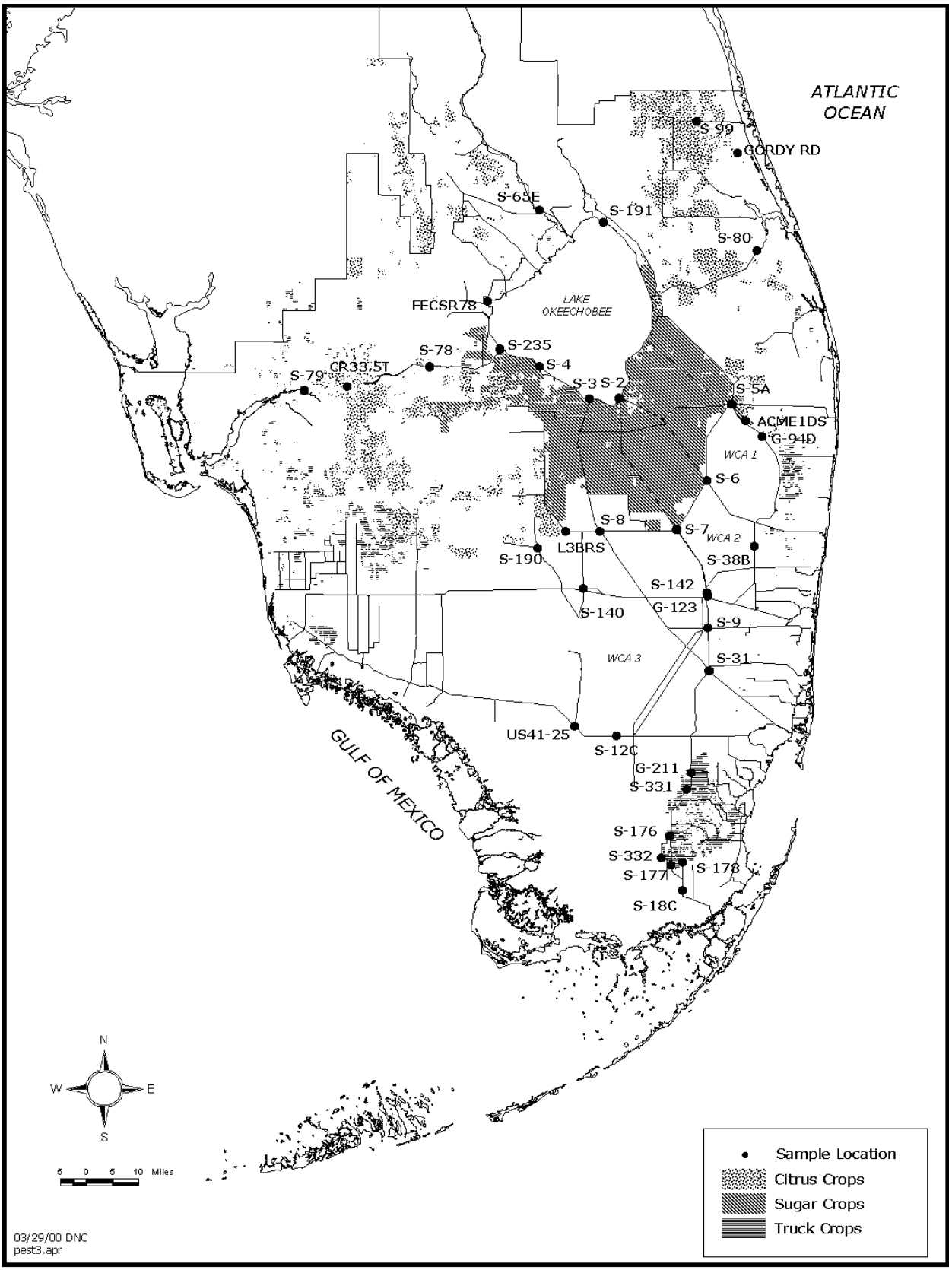

Figure 1. SFWMD Pesticide Monitoring Network

Table 1. Minimum detection limits (MDL) and practical quantitation limits (PQL) for pesticides determined in November 2000.

Pesticide or metabolite	Water range of MDL-PQL (µg/L)	Sediment range of MDL-PQL (µg/Kg)	Pesticide or metabolite	Water range of MDL-PQL (µg/L)	Sediment range of MDL-PQL (µg/Kg)
2,4-D	0.8 - 1.6	33 - 500	endosulfan sulfate	0.0018 - 0. 008	0.81 - 64
2,4,5-T	0.8 - 1.6	33 - 500	endrin	0.0018 - 0. 008	1. 6 - 128
2,4,5-TP (silvex)	0.8 - 1.6	33 - 500	endrin aldehyde	0.0018 - 0. 008	0.81 - 33.2
Alachlor	0.047 - 0.196	24 - 440	ethion	0.019 - 0. 08	2 - 48
Aldrin	0.00094 - 0.004	0.4 - 31.6	ethoprop	0.019 - 0. 08	4 - 96
Ametryn	0.0094 - 0.0392	2 - 48	fenamiphos (nemacur)	0.028 - 0.116	17 - 380
Atrazine	0.0094 - 0.076	2 - 48	fonofos (dyfonate)	0.019 - 0.08	4 - 96
atrazine desethyl	0.0094 - 0.0392	NA	heptachlor	0.00093 - 0.004	0.4 - 31.6
atrazine desisopropyl	0.0094 - 0.0392	NA	heptachlor epoxide	0.00092 - 0.004	0.4 - 31.6
azinphos methyl (guthion)	0.019 - 0. 08	2 - 48	hexazinone	0.019 - 0.08	3.4 - 192
α-BHC (alpha)	0.00092 - 0.004	0.48 - 31.6	imidacloprid	0.2 - 0.4	NA
β-BHC (beta)	0.0018 - 0. 008	0.4 –31.6	linuron	0.2 - 0.4	8.1 - 95
δ-BHC (delta)	0.00092 - 0.004	0.81 - 64.	malathion	0.028 - 0.116	6 - 144
γ-BHC (gamma) (lindane)	0.00093 - 0.004	0.4 - 31.6	metalaxyl	0.047 - 0.196	NA
Bromacil	0.038 - 0.156	16 - 380	methamidophos	NA	20 - 480
Butylate	0.019 - 0.08	NA	methoxychlor	0.0037 - 0.016	2 - 160
carbophenothion (trithion)	0.028 - 0.12	2 - 48	metolachlor	0.057 - 0.236	20 - 480
Chlordane	0.0092 - 0. 04	6 - 144	metribuzin	0.019 - 0.08	4 - 96
Chlorothalonil	0.018 - 0.08	2 - 48	mevinphos	0.057 - 0.236	8.1- 192
chlorpyrifos ethyl	0.019 - 0.08	2 - 48	mirex	0.0018 - 0.008	1.6 - 38
chlorpyrifos methyl	0.0094 - 0.0392	4.1 - 230	monocrotophos (azodrin)	NA	40 - 960
Cypermethrin	0.0046 - 0.02	NA	naled	0.075 - 0.312	33 - 760
DDD-p,p’	0.0019 - 0.008	0.81 - 64	norflurazon	0.019 - 0.08	4 - 96
DDE-p,p’	0.0018 - 0.008	0.81 - 64	parathion ethyl	0.019 - 0.08	6 - 144
DDT-p,p’	0.0018 - 0.008	1.2 - 96	parathion methyl	0.019 - 0.08	6 - 144
Demeton	0.11 - 0.48	40 - 960	PCB	0.018 - 0.08	8.8 - 440
Diazinon	0.019 - 0.08	4 - 96	permethrin	0.047 - 0.02	NA
dicofol (kelthane)	0.018 - 0.08	6 - 144	phorate	0.028 - 0.116	2.0 - 48
Dieldrin	0.0018 - 0.008	0.4 - 31.6	prometryn	0.019 - 0.08	6 - 144
Disulfoton	0.019 - 0.08	4 - 96	simazine	0.0094 - 0.0392	2.0 - 48
Diuron	0.2 - 0.4	8.1 - 95	toxaphene	0.069 - 0.3	30 - 420
α-endosulfan (alpha)	0.0018 - 0.008	0.4 - 31.6	trifluralin	0.0092 - 0.04	1.8 - 38
β-endosulfan (beta)	0.0018 - 0.008	0.4 - 31.6	zinc phosphide	0.05 – 2.0	NA

NA – not analyzed

Table 2. Summary of pesticide residues above the method detection limit found in surface water samples collected by SFWMD in November 2000.

DATE	SITE	FLOW	COMPOUNDS (µg/L)											Number of compounds detected at site
			ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	alpha endosulfan	ethion	ethoprop	hexazinone	norflurazon	simazine	
11/13/00	S18C	N	-	0.011 I	-	-	-	0.0074 I	-	-	-	-	-	2
	S178	N	-	0.027 I	-	-	-	0.0028 I	-	-	-	-	-	2
	S177	Y	-	0.010 I	-	-	-	0.0043 I	-	-	-	-	-	2
	S332	N	-	0.027 I	-	-	-	0.0040 I	-	-	-	-	-	2
	S176	N	-	0.010 *I	-	-	-	-	-	-	-	-	-	1
11/14/00	US41-25	N	-	-	-	-	-	-	-	-	-	-	-	0
	S12C	Y	-	-	-	-	-	-	-	-	-	-	-	0
	S31	N	-	-	-	-	-	-	-	-	-	-	-	0
	S9	N	-	-	-	-	-	-	-	-	-	-	-	0
	S331	Y	-	-	-	-	-	-	-	-	-	-	-	0
	G211	Y	-	-	-	-	-	-	-	-	-	-	-	0
	S99	N	-	-	-	0.012 I	0.061 I	-	0.026 I	-	-	0.74	0.062	5
	GORDYRD	N	-	-	-	0.015 I	0.069 I	-	-	-	-	0.74	0.11	4
	S80	N	-	-	-	-	0.085 I	-	-	-	-	0.48	0.10	3
	S2	N	0.018 *I	0.11 *	0.023 *I	-	-	-	-	-	-	-	0.014 *I	4
	S3	N	0.015 I	0.15	0.034 I	0.011 I	0.056 I	-	-	-	-	-	0.025 I	6
	S4	N	0.013 I	0.13	0.032 I	0.011 I	0.049 I	-	-	-	-	-	0.025 I	6
11/15/00	S140	N	-	-	-	-	-	-	-	-	0.061 I	0.041 I	0.014 I	3
	S190	N	-	-	-	-	0.057 I	-	-	-	-	0.087	-	2
	G123	N	-	-	-	-	-	-	-	-	-	-	-	0
	S142	N	-	-	-	-	-	-	-	-	-	-	-	0
	S38B	N	0.014 *I	1.4 *	0.096 *	-	-	-	-	-	-	-	-	3
	S79	N	-	0.043	-	-	1.1	-	-	-	-	0.38	0.18	4
	CR33.5T	Y	-	0.092	-	-	1.5	-	-	-	-	0.49	0.11	4
	S78	N	0.028 I	0.26	0.021 I	-	-	-	-	-	0.026 I	0.31	0.019 I	6
	S235	N	0.022 *I	0.10 *	0.019 *I	-	0.065 *I	-	-	-	-	0.036 *I	0.068 *	6
	FECSR78	N	-	-	-	-	-	-	-	-	-	-	-	0
	S65E	N	-	-	-	-	0.079 I	-	-	-	-	0.020 I	0.036 I	3
	S191	N	-	-	-	-	0.044 I	-	-	-	0.025 I	0.028 I	0.026 I	4
11/16/00	L3BRS	N	0.011 I	-	-	-	-	-	-	-	-	-	-	1
	S8	N	0.021 I	0.027 I	-	-	-	-	-	-	-	-	-	2
	S7	R	0.010 *I	-	-	-	-	-	-	-	-	-	-	1
	S6	N	0.062	0.013 I	-	-	-	-	-	0.041 I	-	-	-	3
	S5A	N	0.045	0.043	-	-	-	-	-	-	-	-	0.27	3
	ACME1DS	N	0.039	-	-	-	-	-	-	-	-	-	-	1
	G94D	N	0.035 I	-	-	-	-	-	-	-	-	-	-	1
Total number of compound detections			13	16	6	4	11	4	1	1	3	11	14	

N – no Y – yes R – reverse ; - denotes that the result is below the MDL; * - results are the average of duplicate samples; I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 3. Summary of pesticide residues above the method detection limit found in sediment samples collected by SFWMD in November 2000

DATE	SITE	COMPOUNDS (µg/Kg)							Number of compounds Detected at Site
		aldrin	ametryn	DDD	DDE	DDT	Ethion	PCB-1254	
11/13/00	S177	-	-	-	8.9	-	-	-	1
11/14/00	S331	-	-	-	3.1 I	-	-	-	1
	S31	-	-	-	3.8 I	-	-	-	1
	G211	-	-	-	4.0 I	-	-	-	1
	S3	-	-	5.1 I	-	-	-	-	1
	S4	-	20 I	-	-	-	-	-	1
	S80	-	-	-	8.4 I	-	-	-	1
	S99	-	-	-	1.4 I	-	9.2 I	-	2
11/15/00	S79	-	-	-	17 I	-	-	170 I	2
	S190	-	-	-	1.9 I	-	-	28 I	2
	S142	-	-	-	3.0 I	-	-	-	1
11/16/00	ACMEIDS	0.83 I	-	3.0 I	7.9	-	-	-	3
	S5A	-	-	34 I	75	3.2 I	-	-	3
	S6	-	21 I	64 I	260	8.5 I	-	-	4
	L3BRS	-	-	-	2.8 I	-	-	-	1
	S8	-	4.7 I	-	4.3	-	-	-	2
Total number of compound detections		1	3	4	14	2	1	2	

- denotes that the result is below the MDL; * - results are the average of duplicate samples; I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 4. Selected properties of pesticides found in the November 2000 sampling event.

Common name	FDEP Surface Water Standards 62-302 (µg/L)	Florida Ground Water Guidance Conc. (µg/L)	LD_{50} acute rats oral (mg/Kg) (1)	EPA Carcinogenic Potential	Water Solubility (mg/L) (2, 3)	Koc (ml/g) (2, 3)	soil half-life (days) (2, 3)	SCS rating (2) LE	SA	SS	Bioconcentration Factor (BCF)
aldrin	3	0.05	38-67	B2	0.05	48500	-	-	-	-	3348
ametryn	-	63	1,110	D	185	300	60	M	M	M	33
atrazine	-	3**	3,080	C	33	100	60	L	M	L	86
bromacil	-	90	5,200	C	700	32	60	L	M	M	15
DDD-P,P'	-	0.1	3,400	-	0.055	239,900	-	-	-	-	3,173
DDE-P,P'	-	0.1	880	-	0.065	243,220	-	-	-	-	2,887
DDT-P,P'	0.001	0.1	113	-	0.00335	140,000	-	-	-	-	15,377
endosulfan, alpha	0.056	0.35	70	-	0.53	12400	50	XS	L	M	884
ethion	-	3.5	208	-	1.1	8900	150	S	L	M	586
ethoprop	-	-	62	-	750	70	25	L	S	M	15
hexazinone	-	231	1,690	D	33,000	54	90	L	M	M	2
norflurazon	-	280	9,400	C	28	700	90	M	M	L	94
PCB1254	0.014	0.5**	-	B2	-	-	-	-	-	-	-
simazine	-	4**	>5,000	C	6.2	130	60	L	M	M	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large (L), medium (M), small (S) or extra small (XS)
Bioconcentration Factor (BCF) calculated as BCF = 10^(2.791 - 0.564 log WS) (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP surface water standards (12/96) for Class III water except Class I in ( )
**primary standard

(1) Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.
(2) Goss, D. and R. Wauchope. (Eds.) (1992). The SCS/ARS/CES Pesticide Properties Database: II Using It With Soils Data In A Screening Procedure. Soil Conservation Service. Fort Worth, TX.
(3) Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, MI.
(4) Lyman,W.J., W.F. Reehl, and D.H. Rosenblatt. (1990). Handbook of Chemical Property Estimation Methods. American Chemical Society, Washington, DC.
(5) U.S. Environmental Protection Agency (1996). Drinking Water Regulations and Health Advisories. Office of Water. EPA 822-B-96-002.

Table 5. Toxicity of pesticides found in the November 2000 sampling event to selected freshwater aquatic invertebrates and fishes (ug/L).

Common name	48 hr EC_{50} Water flea *Daphnia Magna*		acute toxicity (*)	chronic toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales Promelas*		acute toxicity	chronic toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*		acute toxicity	chronic toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*		acute toxicity	chronic toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*		acute toxicity	chronic toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*		acute toxicity	chronic toxicity
aldrin	-		-	-	28	(5)	9.3	1.4	13	(5)	4.30	0.65	-		-	-	17.7	(5)	5.9	0.89	-		-	-
ametryn	28,000	(6)	9,333	1,400	-		-	-	4,100	(4)	1,367	205	-		-	-	8,800	(4)	2,933	440	-		-	-
atrazine	6,900	(6)	2,300	345	15,000	(6)	5,000	750	16,000	(4)	5,333	800	-		-	-	8,800	(4)	2,933	440	7,600	(4)	2,533	380
bromacil	-		-	-	-		-	-	127,000	(6)	42,333	6,350	-		-	-	36,000	(6)	12,000	1,800	-		-	-
DDD-P,P'	3,200	(7)	1,067	160	4,400	(1)	1,467	220	42	(1)	14	2.1	42	(1)	14	2.1	70	(1)	23.3	3.5	1,500	(1)	500	75
DDE-P,P'	-		-	-	-		-	-	240	(1)	80	12	-		-	-	32	(1)	10.7	1.6	-		-	-
DDT-P,P'	-		-	-	-		-	-	8	(5)	2.7	0.4	2	(5)	0.7	0.1	7	(5)	2.3	0.35	16	(5)	5.3	0.8
endosulfan	166	(6)	55	8	1	(1)	0.33	0.05	1	(1)	0.33	0.05	-		-	-	1	(1)	0.33	0.050	1	(1)	0.3	0.05
	-		-	-	-		-	-	2	(3)	0.67	0.10	-		-	-	3	(2)	1	0.15	1.5	(6)	0.5	0.08
	-		-	-	-		-	-	-		-	-	-		-	-	1	(3)	0.33	0.050	-		-	-
	-		-	-	-		-	-	-		-	-	-		-	-	0.3	(5)	0.10	0.015	-		-	-
ethion	0.06	(1)	0.02	0.003	720	(1)	240	36	210	(1)	70	11	173	(1)	58	9	500	(1)	167	25	7,600	(1)	2,533	380
	-		-	-	-		-	-	13	(3)	4.3	0.65	150	(8)	50	8	193	(3)	64	10	7,500	(8)	2,500	375
	-		-	-	-		-	-	22	(8)	7.3	1.1	-		-	-	560	(8)	187	28	-		-	-
ethoprop	93	(6)	31	4.7	-		-	-	-		-	-	-		-	-	13,800	(4)	4600	690	-		-	-
hexazinone	151,600	(6)	50,533	7,580	274,000	(4)	91,333	13,700	100,000	(6)	33,333	5,000	-		-	-	180,000	(6)	60,000	9,000	-		-	-
norflurazon	15,000	(6)	5,000	750	-		-	-	16,300	(6)	5,433	815	-		-	-	8,100	(6)	2,700	405	>200,000	(4)	>67,000	>10,000
simazine	1,100	(6)	367	55	100,000	(6)	33,333	5,000	90,000	(4)	30,000	4,500	-		-	-	100,000	(6)	33,333	5,000	-		-	-

(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC_{50} is the lowest value which has been determined for a species significant to the indigenous aquatic community.

(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson, W. W. and M.T. Finley (1980). Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. U.S. Department of the Interior, Fish and Wildlife Service Resource Publication 137. Washington, DC.

(2) U.S. Environmental Protection Agency (1977). Silvacultural Chemicals and Protection of Water Quality. Seattle, WA. EPA-910/9-77-036.

(3) Schneider, B.A. (Ed.) (1979). Toxicology Handbook, Mammalian and Aquatic Data, Book 1: Toxicology Data. U.S. Environmental Protection Agency. U.S. Government Printing Office. Washington, DC. EPA-5400/9-79-003

(4) Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.

(5) Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, MI.

(6) U.S. Environmental Protection Agency (1991) Pesticide Ecological Effects Database, Ecological Effects Branch, Office of Pesticide Programs, Washington, D.C.

(7) Verschueren, K. (1983). Handbook of Environmental Data on Organic Chemicals. Second Edition, Van Nostrand Reinhold Co. Inc., New York N.Y.

(8) U.S. Environmental Protection Agency (1972). Effects of Pesticides in Water: A Report to the States. U.S. Government Printing Office. Washington, D.C.

(9) Mayer, F.L., and M.R. Ellersieck. (1986). Manual of Acute Toxicity: Interpretation and Database for 410 Chemicals and 66 Species of Freshwater Animals. U.S. Fish and Wildlife Service, Publication No. 160

Table 6. Atrazine Desethyl/Atrazine Ratio (DAR) Data.

DATE	SITE	FLOW*	atrazine ug/l	moles/l	atrazine desethyl ug/l	moles/l	DAR
11/14/00	S2	N	0.11**	5.10003E-10	0.023**	1.22581E-10	0.2
	S3	N	0.15	6.95458E-10	0.034	1.81206E-10	0.3
	S4	N	0.13	6.02731E-10	0.032	1.70547E-10	0.3
11/15/00	S38B	N	1.4**	6.49094E-09	0.096**	5.11641E-10	0.1
	S78	N	.26	1.20546E-09	0.021	1.11922E-10	0.1
	S235	N	0.10**	4.63639E-10	0.019**	1.01262E-10	0.2

DAR	all sites	flow only sites	no flow sites
average	0.2		0.2
median	0.2		0.2
minimum	0.1		0.1
maximum	0.3		0.3

* N – no Y – yes R- reverse **Average

Figure 2. Ethion Concentration in Surface Water at S99

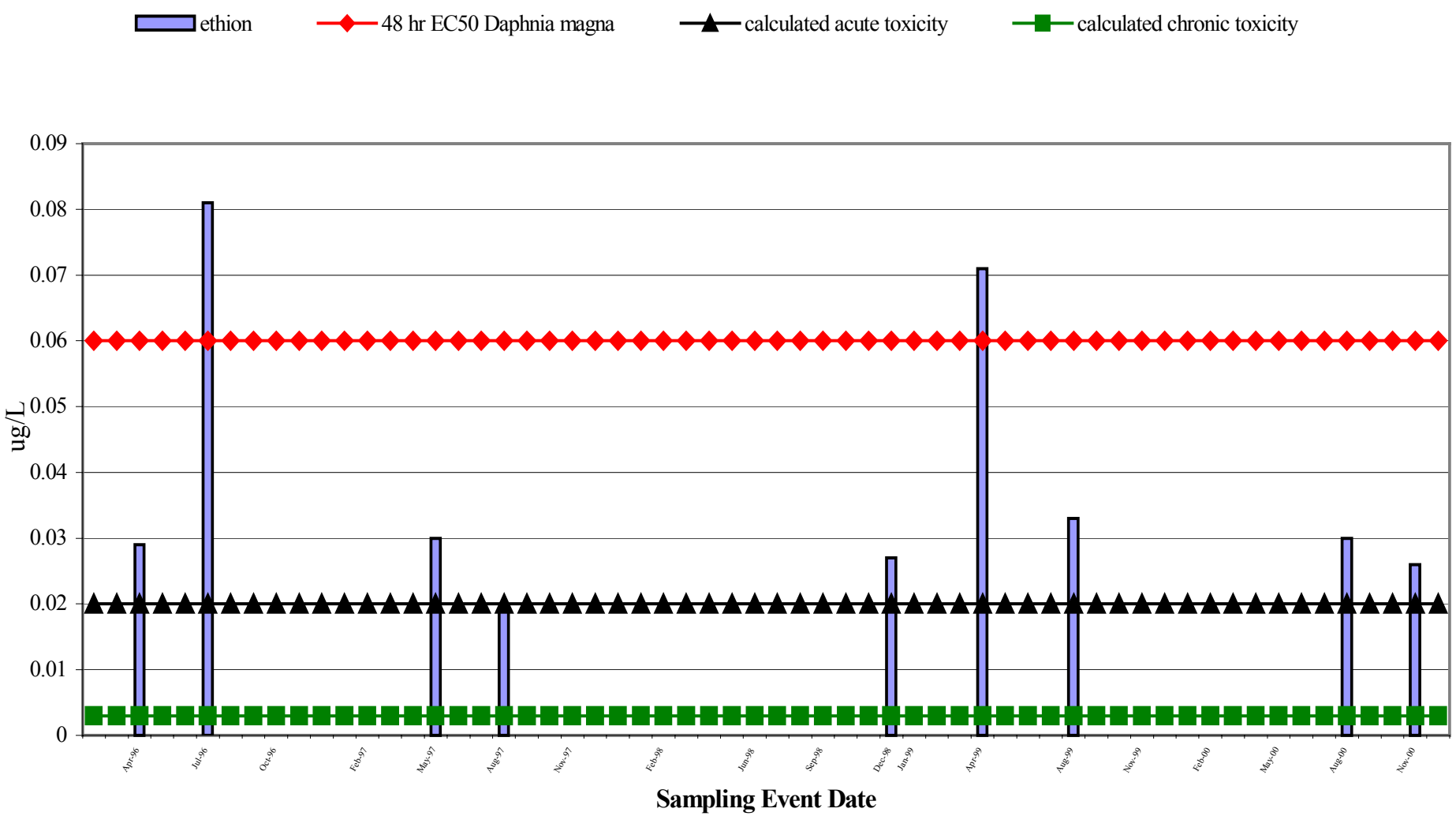

Figure 3. Endosulfan Concentration in Surface Water at S178